Reactions of Bis[pentane-2,4-dionato]cobalt(II) with Alkyl Halides

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The alkylations of pentane-2,4-dione (acetylacetone) by activation through its transition metal complexes offer some advantages over the classical methods based on the use of alkaline media. We have undertaken a general study to explore those advantages and our previous results with bis[pentane-2,4-dionato]nickel(II) proved to be promising[1]. Now we have broadened the scope of our method. Pentane-2,4-dione can be *C*-alkylated with sterically hindered alkyl halides and/or halides which are known to undergo usually elimination of hydrogen bromide more readily than substitution when activated in the form of its cobalt(II) complex [Co(acac)$_2$].

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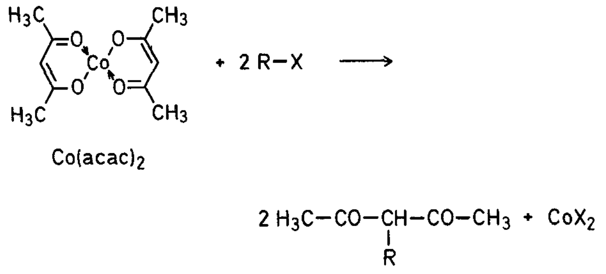

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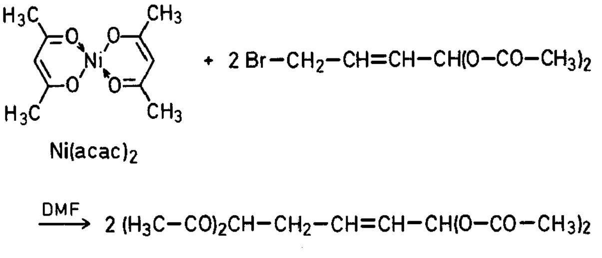
All the successfully tested alkyl halides have the common feature of being precursors of stabilized carbenium ions. Entry 5 deserves particular mention, since 2-bromo-2-phenylpropane spontaneously loses hydrogen bromide. 2-Phenylpropene and its dimer 2,4-diphenyl-4-methylpent-1-ene[9] were also isolated from the reaction mixture.

Other alkyl halides lead to less satisfactory results. Thus, 4-bromo-1,1-diacetoxybut-2-ene, with a strong electron-attracting functionality at the double bond, does not react with Co(acac)$_2$ in chloroform and gives only 8% of *C*-monoalkylation product (entry 8) when dimethylformamide is the solvent. However, this alkyl halide produces a 53% yield of 3-acetyl-7,7-diacetoxybut-5-en-2-one (**1h**) upon reaction with bis[pentane-2,4-dionato]nickel(II) in dimethylformamide at 80°.

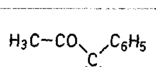
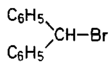
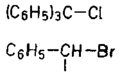
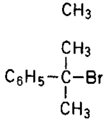
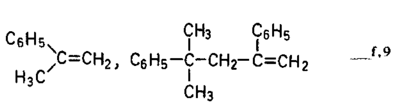
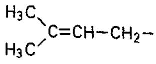
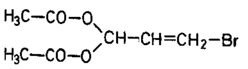
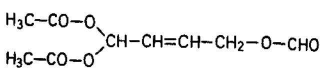


1h

Thus, the cobalt(II) and nickel(II) complexes complement each other in their alkylating abilities[1].

When chloromethoxymethane was made to react with Co(acac)$_2$ in chloroform, no *C*-alkylation product was produced. Instead, mixtures of 2-methoxymethoxy-4-oxo-2-pentene (**2**) and 3,5-diacetylheptane-2,6-dione[10] (**3**) were formed. We have shown that product **3** arises from hydrolysis of the unstable **2**.

Table. Reactions of Alkyl Halides with Cobalt Acetylacetonate in Chloroform

Entry	Alkyl halide	Product[a]	Reaction conditions time/temperature	Yield [%]	b.p./torr or m.p.	Molecular formula or Lit. b.p./torr or m.p.	Other products	Yield [%]
1	$C_6H_5-CH_2-Br$	**1a**	20 h/reflux	53	65–75°/0.2	135–136°/7[2]	 $(H_3C-CO)_2C(C_6H_5)_2$	14[b]
2	 $(C_6H_5)_2CH-Br$	**1b**	17 h/reflux	97	113–115°	116°[4]	—	—
3[c]	$(C_6H_5)_3C-Cl$	**1c**	3 h/reflux	29	167.5–168.5°	170–171.5°[5]	Co(acac)$_3$, $(C_6H_5)_3CH$, $(C_6H_5)_3C-OH$	—
4	 $C_6H_5-CH(CH_3)-Br$	**1d**	15 h/reflux	94	101–105°/0.5 (48–49°)	111–114°/2[6] (48.2–48.8°)[d]	—	—
5	 $C_6H_5-C(CH_3)_2-Br$	**1e**	24 h/r.t.	14	oil[e,f]	$C_{14}H_{18}O_2$ (218.3)	 $(C_6H_5)(H_3C)C=CH_2$, $C_6H_5-C(CH_3)_2-CH_2-C(C_6H_5)=CH_2$	—[f,9]
6[c]	$t-C_4H_9-Br$	**1f**	76 h/reflux	4	110°/15[g]	76–79°/11[7]	$(H_3C-CO)_2CH_2$	
7	 $(H_3C)_2C=CH-CH_2-Cl$	**1g**	15 h/reflux	76	120°/15[g]	107–108°/33[8]	—	
8[h]	 $(H_3C-CO-O)_2CH-CH=CH_2-Br$	**1h**	24 h/90°	8	140°/0.3[g]	$C_{13}H_{18}O_6$ (270.3)[i]	 $(H_3C-CO-O)_2CH-CH=CH-CH_2-O-CHO$	
9	H_3CO-CH_2-Cl	**2**	4.5 h/−15°	24	see text	—	**3**	40
10	H_3CO-CH_2-Cl	—	3 h/r.t.	—	see text	—	**3**	74

[a] All compounds prepared showed the expected spectral characteristics.

[b] m.p. 112–114° (Lit. [3] m.p. 113°).

[c] Excess alkyl halide used.

[d] Bis[2,4-dinitrophenylhydrazone] has m.p. 260–261.5° (Lit. [6] m.p. 267–269°).

[e] Bis[2,4-dinitrophenylhydrazone] has m.p. 211–213°.

$C_{26}H_{26}N_8O_8$	calc.	C 53.99	H 4.53	N 19.37
(578.5)	found	53.74	4.51	19.45

[f] Purified by column chromatography on silica gel.

[g] Oven temperature.

[h] In dimethylformamide.

[i]

$C_{13}H_{18}O_6$	calc.	C 57.77	H 6.71
(270.3)	found	57.73	6.75

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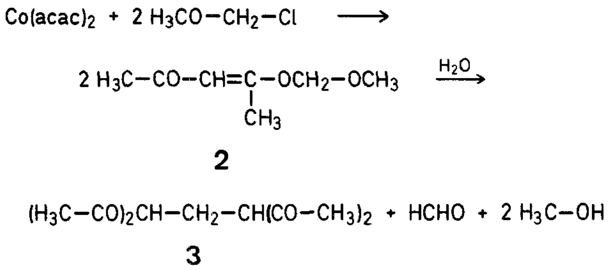

$$Co(acac)_2 + 2\,H_3CO-CH_2-Cl \longrightarrow$$

$$2\,H_3C-CO-CH=\underset{CH_3}{\underset{|}{C}}-OCH_2-OCH_3 \xrightarrow{H_2O}$$

2

$$(H_3C-CO)_2CH-CH_2-CH(CO-CH_3)_2 + HCHO + 2\,H_3C-OH$$

3

Preference for *O*- vs. *C*-alkylation is well documented for hard electrophiles[11].

To assess the usefulness of our method, some comparisons with the classical ones should be made. 3-Diphenylmethylpentane-2,4-dione (**1b**) has been previously prepared, without yield specification, by the reaction of diphenylmethanol with pentane-2,4-dione[4]. 3-Triphenylmethylpentane-2,4-dione (**1c**) has been synthesized through a very sophisticated way[5]. The authors state that they "have been unable to obtain this compound either by the reaction of triphenylmethanol with acetylacetone alone or in the presence of fluoroboric acid or organic bases". 3-(1-Phenylethyl)pentane-2,4-dione (**1d**) has been synthesized in 28 % yield, by using the sodium salt of pentane-2,4-dione[6]. 3-(2-Phenyl-2-propyl)-pentane-2,4-dione (**1e**) was unknown. 3-*t*-Butylpentane-2,4-dione (**1f**) can be prepared by a synthesis based on the use of isobutylene in acid medium[7]. 3-(3-Methylbut-2-enyl)-pentane-2,4-dione has been prepared by treatment of 3-methylbut-2-enyl bromide with the sodium salt of pentane-2,4-dione in dimethylformamide[8], although in only 34% yield.

Further research is under way to broaden the scope of our method, but we can anticipate that it can be considered as an alternative to the conventional ones.

3-(1-Phenylethyl)-pentane-2,4-dione, (1d); Typical Procedure:

A mixture of 1-bromoethylbenzene (1.43 g, 7.74 mol) and cobalt acetylacetonate (1.00 g, 3.89 mmol) in ethanol-free chloroform (25 ml) is heated under reflux for 15 h. A precipitate forms and is filtered off. The liquid is washed with water, dried, and evaporated to yield a greenish residue which is purified by silica gel column chromatography [CCl_4/CH_2Cl_2 (1:1)]. The product crystallizes spontaneously to give **1d**; yield: 1.47 g (94 %); m.p. 48–49° (Lit. [6] m.p. 48.2–48.8°).

2-Methoxymethoxy-4-oxo-2-pentene (2) and 3,5-Diacetylheptane-2,6-dione (3):

A mixture of chloromethoxymethane (1.57 g, 19.5 mmol) and cobalt acetylacetonate (5.0 g, 19.5 mmol) in ethanol-free chloroform (30 ml) is stirred at room temperature for 5.5 h. The liquid is washed with water, dried, and evaporated. The residue is purified by silica gel column chromatography to give **2** [ether/CH_2Cl_2 (1:3)] as an oil; yield: 0.72 g (26%); and **3**.

^{1}H-N.M.R. ($CDCl_3$): $\delta = 2.15$ (s, 3H); 2.30 (s, 3H); 3.45 (s, 3H); 5.05 (s, 2H); 5.70 ppm (s, 1H).

M.S. (70 eV): $m/e = 144$ (M^+, 83 %); 129 (79 %); 113 (100 %); 112 (59 %); 111 (22 %); 101 (40 %); 100 (23 %); 97 (25 %); 85 (25 %); 83 (20%); 71 (17%); 55 (22%); 43 (86%).

Compound **3** [ether/CH_2Cl_2 (1:1)]; yield: 1.31 g (35 %). Product **3** is converted to bis[4-pyrazolyl]methane according to Lit.[10]; m.p. 281–284° (Lit.[10]; m.p. 285–287°). Distillation of **2** at water pump pressure gives some **3**; b.p. 130–140° (oven temp.) and a dark residue remains in the distillation flask.

A reaction performed at −15° gives the yields reported in the Table as determined by ^{1}H-N.M.R. analysis.

Alternatively, a mixture of chloromethoxymethane (0.79 g, 9.7 mmol) and cobalt acetylacetonate (1.25 g, 4.9 mmol) in ethanol-free chloroform (30 ml) is stirred at room temperature for 3 h. The liquid is washed with water, dried, and evaporated to give practically pure **3**; yield: 0.77 g (74 %).

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